

**United States Patent Application for:**

**ELECTROCHEMICALLY ROUGHENED ALUMINUM  
SEMICONDUCTOR PROCESSING APPARATUS SURFACES**

**Inventor: Jennifer Y. Sun  
Clifford C. Stow  
Senh Thach**

**Attorney Docket No. AM-5431**

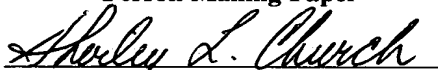
---

**Certification Under 37 CFR 1.10**

I hereby certify that this new Patent Application and the documents referred to as enclosed therein are being deposited with the United States Postal Service on this date July 27, 2001 in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number ET160304673US addressed to the: Commissioner for Patents, Box Patent Application, Washington, DC 20231.

Shirley L. Church, Esq.

Person Mailing Paper

  
Signature of Person Mailing Paper

1 [0001] **ELECTROCHEMICALLY ROUGHENED ALUMINUM**  
2 **SEMICONDUCTOR PROCESSING APPARATUS SURFACES**

3 [0002] **BACKGROUND OF THE INVENTION**

4 [0003] 1. Field of the Invention

5 [0004] The present invention pertains to an electrochemically roughened aluminum or  
6 aluminum alloy surface for use within a semiconductor processing chamber. The present  
7 invention also pertains to a method of electrochemically roughening an aluminum or  
8 aluminum alloy surface. The roughened surface is typically anodized to provide a finished  
9 surface for use in semiconductor processing.

10 [0005] 2. Brief Description of the Background Art

11 [0006] Semiconductor manufacturing processes, such as etch and deposition processes,  
12 utilize a wide variety of processing gases and substrate materials. Highly volatile process  
13 byproducts are typically removed from the processing chamber by application of vacuum.  
14 Less volatile byproducts may adhere to the interior surface of the processing chamber or  
15 may redeposit on the surface of the semiconductor substrate being processed. Most  
16 semiconductor manufacturers prefer to have redepositing byproducts deposit on processing  
17 chamber surfaces (rather than the substrate). The processing chamber surfaces are then  
18 periodically cleaned. Frequent chamber cleanings are expensive in terms of processing  
19 chamber downtime. The more redeposited byproducts which can be held by the processing  
20 chamber surfaces, the less frequent the cleaning requirement.

21 [0007] Interior surfaces of semiconductor processing chambers are frequently aluminum.  
22 One prior art semiconductor processing chamber includes anodized aluminum surfaces  
23 which have been lapped to have a surface roughness of only 4 Ra, which is essentially a  
24 mirror finish. However, when subjected to the high temperatures and processing conditions  
25 used in many semiconductor manufacturing processes, the highly polished, anodized

1 aluminum surface developed numerous tiny cracks in the anodized layer, known as craze  
2 lines; these are shown in Figure 1. While the craze lines 100 typically do not penetrate all  
3 of the way through the anodized layer to the boundary layer at the base aluminum beneath,  
4 they tend to spread across the anodized surface, producing a spider web pattern. During a  
5 fluorine-based etch process, the anodized aluminum surface reacts with fluorine gas, causing  
6 the craze lines to fill with a self-passivating fluoride. Although the craze lines may not  
7 interfere with the operation of the chamber during a fluorine-based etch process, they are  
8 cosmetically unappealing, and the user of the processing chamber tends to worry that  
9 fluorine-containing species may be passing through the protective anodized layer and  
10 corroding the aluminum surface beneath. Further, in a non-fluorine-based environment  
11 (such as during a chlorine-based etch process), the craze lines do not fill with self-  
12 passivating fluoride and the anodized surface may eventually fail, exposing the aluminum  
13 beneath to corrosion by chlorine-containing species.

14 [0008] During a number of semiconductor processing procedures, byproducts are formed  
15 which are not sufficiently volatile to be removed by the vacuum system of the processing  
16 chamber. In many instances, it is desirable to provide a surface inside the processing  
17 chamber on which these byproducts are capable of adhering, so that they will not fall upon  
18 semiconductor workpieces during processing, causing contamination.

19 [0009] One method of improving the adhesion of semiconductor processing byproducts  
20 to an aluminum surface within a semiconductor processing chamber is to provide a  
21 roughened surface to which byproducts generated during processing can stick. Typically,  
22 aluminum semiconductor chamber surfaces have been roughened by bead blasting.  
23 However, bead blasting often is a manual process, in which it is difficult to control the  
24 uniformity and repeatability. Further, bead blasting typically provides a very sharp, jagged  
25 surface 200 on the aluminum, as shown in Figure 2. Tips of the roughened aluminum can  
26 curl over, forming hook-shaped projections 202 which can break off or entrap particles 204,

1 including the bead blast particle itself. As a result, the bead blasting media may act as a  
2 source of contamination of the aluminum surface. Bead blasting is not useful as a  
3 roughening method for some of the softer aluminum alloys, such as the 1000 series, because  
4 the bead blasting particles can easily become embedded in the ductile metal. Further, the  
5 sharp surface provided by bead blasting may complicate a subsequent anodization process.

6 [0010] It would therefore be desirable to provide a uniform and controllable method for  
7 roughening an aluminum surface which could be used for all aluminum alloys. In particular,  
8 the roughening method should provide a surface which does not entrap particles, is free from  
9 jagged and hooked surface formations, and is easily anodized.

10 [0011] **SUMMARY OF THE INVENTION**

11 [0012] Applicants have discovered a uniform, controllable method for electrochemically  
12 roughening an aluminum-comprising surface intended for use within a semiconductor  
13 processing chamber. Typically the aluminum-comprising surface is aluminum or an  
14 aluminum alloy. Applicants have also determined that if they electrochemically roughen an  
15 aluminum or aluminum alloy surface, they avoid the formation of jagged and hooked surface  
16 topography. The surface which is formed by the electrochemical roughening provides a  
17 topography which resembles small rolling hills and valleys. The estimated average height  
18 of the hills above the valleys is approximately 16  $\mu\text{m}$ ; the estimated average distance  
19 between the hills is approximately 50  $\mu\text{m}$ , depending on the grade of the aluminum.  
20 Typically, the height of the hills ranges from about 8  $\mu\text{m}$  to about 25  $\mu\text{m}$ , and the distance  
21 between the center of one hill and that of an adjacent hill ranges from about 30  $\mu\text{m}$  to about  
22 100  $\mu\text{m}$ .

23 [0013] Surprisingly, the hill and valley topography obtained by electrochemically  
24 roughening an aluminum or aluminum alloy surface relieves stress in an anodized finish  
25 subsequently produced over the roughened surface, so that the anodized layer does not crack

1 upon thermal cycling up to about 300°C. In addition, unexpectedly, the amount of  
2 redepositing byproduct which can be accumulated over the hills and valleys (including an  
3 anodized surface which mirrors the underlying aluminum surface) is drastically increased  
4 over that which can be accumulated over a bead-blasted surface. As a result, the number of  
5 substrate processing cycles prior to cleaning with the new, electrochemically roughened,  
6 aluminum or aluminum alloy anodized surface is about 5 times greater than with the bead  
7 blasted aluminum anodized surface. [0014] Applicants' method for surface roughening can  
8 be used on aluminum and aluminum alloys in general, including but not limited to 6061 and  
9 LP (available from Alcan Alusuisse). Applicants' method promotes formation of a smooth,  
10 rolling-hilled, anodized surface which does not entrap particles. Further, applicants'  
11 electrochemically roughened aluminum-comprising surfaces provide increased surface area  
12 for collection of redepositing byproducts.

13 [0015] **BRIEF DESCRIPTION OF THE DRAWINGS**

14 [0016] Figure 1 shows a prior art anodized aluminum surface 100 which has been lapped  
15 to have a surface roughness of 4 Ra. Note the many craze lines 102 which have formed in  
16 the aluminum surface subsequent to exposure to process conditions, producing a spider web  
17 pattern.

18 [0017] Figure 2 shows a prior art aluminum surface 200 which has been roughened using  
19 bead blasting. Note the many hook-shaped projections 202 which can break off or entrap  
20 particles 204, including the bead blast particle itself.

21 [0018] Figure 3 shows an aluminum surface 300 which has been roughened using  
22 applicants' electrochemical roughening method. Note the smooth, rolling topography of  
23 applicants' electrochemically roughened aluminum surface.

1        [0019] **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

2        [0020]     Applicants' invention pertains to a method of electrochemically roughening an  
3        aluminum-comprising surface. Typically the aluminum-comprising surface is aluminum or  
4        an aluminum alloy. Aluminum is commonly alloyed with elements such as silicon, copper,  
5        zinc, magnesium, manganese, iron, titanium, and nickel, by way of example, and not by way  
6        of limitation. Applicants' invention has use in semiconductor processing chambers which  
7        include electrochemically roughened aluminum surfaces, and particularly roughened  
8        surfaces having a protective coating thereover, such as an anodized aluminum coating.

9        [0021]     Applicants' method for electrochemically roughening an aluminum-comprising  
10       surface comprises immersing the aluminum-comprising surface in an aqueous HCl solution  
11       having a concentration ranging from about 1 volume % to about 5 volume % at a  
12       temperature ranging from about 45°C to about 80°C, then applying an electrical charge  
13       having a charge density ranging from about 80 amps/ft.<sup>2</sup> to about 250 amps/ft.<sup>2</sup> for a time  
14       period ranging from about 5 minutes to about 25 minutes. Chelating agents (such as, for  
15       example, but without limitation, gluconic acid, available from VWR Scientific Products,  
16       West Chester, PA) may be added to the HCl solution to control the bath chemistry and  
17       conductivity.

18       [0022]     Typical processing conditions for electrochemically roughening aluminum and  
19       aluminum alloys according to applicants' method are presented in Table One, below.

[0023] Table One. Typical Process Conditions for Electrochemically Roughening Aluminum and Aluminum Alloys

Process Parameter	Typical Process Conditions	Preferred Process Conditions	Optimum Known Process Conditions
HCl Concentration (% volume)	1 - 5	1 - 3	1 - 1.5
Chelating Agent (% volume)	0.5 - 3	0.5 - 1.5	0.8 - 1.2
Tank Temperature (°C)	45 - 80	50 - 70	55 - 65
AC Frequency (Hz)	60 - 120	80 - 100	85 - 95
Charge Density (amps/ft. <sup>2</sup> )	80 - 250	120 - 250	150 - 250
Time (min.)	4 - 25	4 - 20	4 - 20

[0024] Processing conditions will need to be adjusted depending on the specific chemical composition of the particular aluminum alloy being roughened. Applicants have performed electrochemical roughening of several commercially available aluminum alloys. Specific processing conditions used during the electrochemical roughening of these alloys are presented in Table Two, below.

[0025] Table Two. Process Conditions for Electrochemically Roughening Particular Aluminum Alloys

Alloy	6061*	LP**
Process Condition		
HCl Concentration (% volume)	1.0 - 1.5	1.0 - 1.5
Gluconic Acid*** (% volume) (Chelating Agent)	0.9 - 1.1	0.9 - 1.1
Tank Temperature (°C)	55 - 65	55 - 65
AC Frequency (Hz)	85 - 95	85 - 95
Charge Density (amps/ft. <sup>2</sup> )	175 - 250	175 - 250
Time (min.)	6 - 12	4 - 8

- 1       \*       Can be obtained from any of the major aluminum manufacturers, such as Alcoa  
2               (Pittsburgh, PA), Alcan, Inc. (Montreal, Canada), and Reynolds Aluminum  
3               Supply Co. (Richmond, VA).  
4       \*\*       Obtained from Alcan Alusuisse (Stegen, Germany).  
5       \*\*\*       Obtained from VWR Scientific Products (West Chester, PA).

6       [0026]   Unroughened, machined aluminum and aluminum alloy typically has a surface  
7       roughness ranging from about 12 Ra to about 32 Ra. After performing applicants'  
8       electrochemical roughening method, the aluminum or aluminum alloy surface typically has  
9       a surface roughness ranging from about 100 Ra to about 200 Ra, preferably ranging from  
10       about 110 Ra to about 160 Ra.

11       [0027]   As shown in Figure 3, applicants' aluminum and aluminum alloy roughening  
12       method provides a surface 300 having a topography resembling small rolling hills and  
13       valleys. The estimated average height of the hills above the valleys is approximately 16  $\mu\text{m}$ ;  
14       the estimated average distance between the hills is approximately 50  $\mu\text{m}$ , depending on the  
15       grade of the aluminum. Typically, the height of the hills ranges from about 8  $\mu\text{m}$  to about  
16       25  $\mu\text{m}$ , and the distance between the center of one hill and that of an adjacent hill ranges  
17       from about 30  $\mu\text{m}$  to about 100  $\mu\text{m}$ . Applicants' electrochemically roughened aluminum or  
18       aluminum alloy surface provides increased surface area for collection of redepositing  
19       byproducts, but does not entrap particles.

20       [0028]   Applicants' electrochemical roughening method is particularly useful for  
21       roughening aluminum and aluminum alloy surfaces which are subsequently protected by a  
22       plasma-resistant coating, for use within semiconductor processing chambers, such as an etch  
23       chamber or a deposition chamber. Applicants' method is particularly useful for roughening  
24       any apparatus surface which comes into contact with semiconductor processing byproducts.  
25       Applicants' electrochemically roughened aluminum or aluminum alloy surface provides  
26       pockets in the hills and valleys which provide for the accumulation of semiconductor  
27       processing byproducts, such as etch byproducts or CVD deposition byproducts, preventing



1 the byproducts from redepositing on the surface of the semiconductor substrate being  
2 processed. It is helpful to use a protective coating applied over the aluminum or aluminum  
3 alloy surface which provides for adhesion of depositing byproducts. Example protective  
4 coatings include anodic oxide, flame spray-deposited aluminum oxide, and other ceramic  
5 coatings which may be conductive or non-conductive.

6 [0029] In particular, during a fluorine-based etch process, fluorine and carbon from the  
7 etch process react to form a polymer which easily adheres to an electrochemically  
8 roughened, anodized aluminum surface.

9 [0030] Applicants' electrochemically roughened, anodized aluminum or anodized  
10 aluminum alloy surfaces can be included in etch chambers which are used for etching  
11 dielectric materials (including inorganic dielectric materials, such as silicon oxide, silicon  
12 nitride, silicon oxynitride, and tantalum pentoxide, and organic dielectric materials, such as  
13 an organic low-k dielectric material), metals (such as aluminum, copper, titanium, tantalum,  
14 and tungsten), and polysilicon, by way of example, and not by way of limitation.

15 [0031] Applicants' method can be used to create roughened surfaces for semiconductor  
16 processing chamber components such as wall liners, cathode liners, slit valve doors, slit  
17 valve liners, buffer inserts, and gas distribution plates, by way of example, and not by way  
18 of limitation.

19 [0032] Anodization of applicants' electrochemically roughened aluminum and aluminum  
20 alloy surfaces can be performed using conventional aluminum anodization techniques  
21 known in the art, such as by following Mil Standard No. A-8625F, by way of example, and  
22 not by way of limitation. Because applicants' roughening method relieves stress within the  
23 aluminum or aluminum alloy surface, the resulting anodized surface does not form craze  
24 lines, even when subjected to the temperature cycling which occurs due to particular  
25 semiconductor manufacturing processes. [0033] Other protective, plasma-resistant  
26 coatings, such as flame spray-deposited aluminum oxide and other ceramic coatings, can be

1 deposited or applied over a roughened aluminum or aluminum alloy surface using  
2 techniques known in the art. Ceramic coatings, either conductive or non-conductive, may  
3 be applied over a roughened, anodized surface.

4 [0034] The above described preferred embodiments are not intended to limit the scope  
5 of the present invention, as one skilled in the art can, in view of the present disclosure  
6 expand such embodiments to correspond with the subject matter of the invention claimed  
7 below.

ET160304673US